

California Environmental Protection Agency

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**Air Resources Board**

Engineering and Laboratory Branch  
Monitoring and Laboratory Division

MLD SOP ES02

STANDARD OPERATION PROCEDURE FOR THE MEASUREMENT OF AMMONIUM  
ION IN AQUEOUS CONSUMER PRODUCTS USING ION SELECTIVE ELECTRODE

March 10, 1998, Revision 2

DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

## **1 INTRODUCTION**

This document describes a method for the determination of ammonia in consumer products. The method is based on Method 350.3, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020 and on "Evaluation of Methods for the Determination of Ammonia in Glass Cleaners and Other Consumer Products", L. Houdashelt, Master's Thesis (1995), University of California, Davis. Ammonia has the potential to be counted as a VOC in the total volatiles analysis as determined by MLD SOP ES01. Ammonium hydroxide, with a vapor pressure of 115 mmHg at 20°C, is present in most glass cleaners and some general purpose cleaners and can potentially cause an overestimation in the VOC determination if not accounted for. The following procedure is designed to quantify ammonia at concentrations equal to or greater than 0.1 % by weight in consumer products. Mention of trade names or commercial products in this procedure are for purposes of demonstration only. Any equivalent product may be used. For more information see ASTM D 1426-93 or U.S EPA Method 300.7.

## **2 SUMMARY OF METHOD**

The Orion Model 920A pH/ISE meter with the Model 95-12 ammonia electrode and Model 900A printer is used for the measurement of dissolved ammonia in aqueous solutions. The ammonium ion, after conversion to ammonia, is measured by the gas-sensing ion selective electrode (ISE) . The sample to be tested is made basic by the addition of an ionic strength adjustment (ISA) solution containing sodium hydroxide and a metals complexing agent, EDTA (ethylenediaminetetraacetic acid). In the presence of basic pH, the ammonium ion in solution is converted to dissolved ammonia which diffuses through the hydrophobic gas-permeable membrane of the electrode. For analysis, a measured amount of product is dissolved in water, ISA solution is added, and the ammonia concentration is determined. A known amount of ammonium ion(spike) is then added to the sample and the concentration determined again. If the recovery of the spike does not fall within  $\pm 10\%$  of the known value, or if the matrix of the product is known to interfere with this procedure, pretreatment may be necessary.

## **3 INTERFERENCES AND LIMITATIONS**

- 3.1 The determination of the dissolved ammonia is affected by the presence of volatile substances, particularly volatile amines, that can diffuse across the membrane and alter the pH of the electrode filling solution. In most cases interference is minimal since an ionic species is formed by the basic solution and therefore impermeable to the membrane.
- 3.2 Complexation of ammonia with metal ions reduces its volatility. The presence of a EDTA in the pH-adjusting ISA solution complexes these metals, freeing the ammonia for analysis.

- 3.3 Reproducibility of the ammonia electrode is limited by temperature fluctuations. A change in temperature can cause the electrode response to shift and change slope. All standards and samples should be maintained at room temperature for analysis, or an automatic temperature compensation probe may be used to reduce the effect of temperature changes. Calibration should be completed every hour to maintain electrode reproducibility of  $\pm 2\%$ .
- 3.4 In a nonaqueous solution or one that contains a surfactant which wets the membrane, the liquid will penetrate the membrane and possibly cause electrode failure. The ammonia electrode should not be immersed in any undiluted consumer product tested that has a high surfactant content.

#### **4 INSTRUMENTATION AND EQUIPMENT**

- 4.1 The Orion Model 920A Advanced pH/ISE meter is used with the Model 95-12 Ammonia electrode and the Orion 900A printer. Refer to the respective instruction manuals for more detailed information on the operation, maintenance, and troubleshooting.
- 4.2 Membranes/ cap for probe (Orion no. 951204 - box of 20 membranes or cat. no. 951205 - bonded membrane cap- 3 per pak).
- 4.3 Stir plate and small magnetic teflon coated stir bars. The stir plate should be maintained at a fixed rate throughout the measurement.
- 4.4 Rainin pipettor, 100 $\mu$ L, 1000 $\mu$ L, 2.5 mL and respective pipets
- 4.5 Beakers, 150 mL
- 4.6 Volumetric flasks, 10 mL, 100 mL

#### **5 REAGENTS AND MATERIALS**

- 5.1 Reagent grade, ASTM Type 1 deionized water, 18.0 M $\Omega$
- 5.2 1-Methoxy-2-propanol (Aldrich #26,889-5) stored over 4A molecular sieves.
- 5.3 Ionic Strength Adjustor (ISA) 5.0 M NaOH/ 0.05 M Disodium EDTA/ 10% Methanol with color indicator (Orion no. 951211).
- 5.4 Internal Filling Solution for the probe (Orion no. 951202)
- 5.5 Ammonium ion standard from Alltech 1000  $\mu$ g/mL NIST-SRM traceable (Alltech cat. no. 37001)

- 5.6 Standard Solutions: Dilute 100  $\mu$ l, 500  $\mu$ l, and 1000  $\mu$ l of the NIST ammonium standard to 100 ml with deionized water. These solutions correspond to 1.0, 5.0, and 10.0  $\mu$ g/ml.
- 5.7 Control Sample: Dilute 500  $\mu$ l of the NIST ammonium standard to 100 ml. This corresponds to a concentration of 5.0  $\mu$ g/ml.

## 6 PROCEDURE

Consult the Orion Model 920A Instruction manual for more complete detail on the operation of the meter. Refer to the instruction manual for the ammonia electrode model 95-12.

- 6.1 Standard and samples should be at the same temperature (room temperature).
- 6.2 The pH-adjusting ISA solution must be added to all standards and samples immediately before measurement. The ISA should bring the pH of the solution in the range of 11-14 (the solution should be blue).
- 6.3 The ammonia is measured in units of  $\mu$ g/mL as  $\text{NH}_4$
- 6.4 Calibration
- 6.4.1 Three calibration standards are made from the 1000  $\mu$ g/mL stock standard. Prepare in a 100mL volumetric flask the standard as follows immediately before analysis:
- |      |                          |               |
|------|--------------------------|---------------|
| 1.0  | $\mu$ g/mL $\Rightarrow$ | 0.1 mL/100 ml |
| 5.0  | $\mu$ g/mL $\Rightarrow$ | 0.5 mL/100 ml |
| 10.0 | $\mu$ g/mL $\Rightarrow$ | 1.0 mL/100 ml |
- 6.4.2 Transfer the 100 mL of the 1.0  $\mu$ g/ml standard into a 150 mL beaker. Place on the stir-plate, place electrode in the beaker. Add 2 mL ISA. Allow the probe to equilibrate to a constant reading. Enter the calculated value for the standard (1.0  $\mu$ g/mL). Remove solution and rinse probe thoroughly.
- 6.4.3 Measure the next two standards in the same manner. After the third calibration standard the meter will automatically determine the calibration factor. The electrode response slope should be in the range of -54 to -60 mV at 20° -25°C.
- 6.4.4 Measure the Control Sample (5.0  $\mu$ g/ml) in the same manner as above. The value of the Control Sample must fall within  $\pm 3s$  of the calculated value.
- 6.5 Sample Measurements

The samples of consumer products are prepared as a 1:10 weight/volume dilution in 1-methoxy-2-propanol (MPA). A 1.0 mL aliquot of the dilution is prepared in a 100 mL

volumetric flask and brought to volume with deionized water. The now 1:1000 dilution of the sample is then analyzed in the same manner as the standards.

- 6.5.1 A weighed aliquot of 1.0 mL of the consumer product sample is diluted to 10 mL with MPA. The sample is transferred to a 10 mL sample vial and capped.
- 6.5.2 A 1.0 mL aliquot of the 1:10 diluted sample is transferred to a 100 mL volumetric flask and brought to volume with deionized water.
- 6.5.3 Place the diluted sample in a 150 mL beaker. Place the electrode in the sample solution and add 2 mL of the ISA. The solution should be blue if it is in the expected pH range (pH 11-14). If the solution is not blue, additional ISA may be added. Wait for a stable reading and record.

#### 6.6 Known Addition

Known addition technique is used to verify the results of the calibration curve and to confirm that nothing is present in the sample matrix that has compromised the integrity of the membrane. The sample potential is measured before and after the addition of a standard solution.

When the sample analyzed has a stable reading, record the ammonium concentration. Pipet 0.5 mL of the 1000  $\mu\text{g/mL}$  stock standard and transfer to the beaker containing the sample and ISA. Wait for a stable reading, the concentration of the solution should be the sample reading plus 5.0  $\mu\text{g/mL}$  for the added standard. If the result does not fall within 0.5  $\mu\text{g/mL}$  of this result, the analysis is discontinued and the cause of the error is corrected.

- 6.7 Store the electrode in deionized water when not in use. Consult the manual for the electrode for longer term storage.

## 7 QUALITY CONTROL

- 7.1 The electrode response is good for ammonia concentrations above 0.07  $\mu\text{g/mL}$ . However, response time is much longer for lower concentrations of ammonia and may not be practical for ammonium concentrations of less than 0.5  $\mu\text{g/mL}$ .
- 7.2 After the calibration, run a reagent blank with the ISA solution. To 100 mL of ASTM Type 1 water add the ISA and measure any ammonia present.
- 7.3 After the calibration, a check should be made with the control sample to evaluate the performance of the meter and then again every 10 samples analyzed and at the end of the analysis. The results of the Control Sample analyses are plotted on the method Control Chart.

- 7.4 A recalibration should be completed every hour to correct for any temperature fluctuations, drifts, or noise.
- 7.5 The weight fraction of ammonium in the liquid product is calculated as follows:

$$\text{Wt. fraction NH}_4 = \frac{(\text{Measured Concentration, } \mu\text{g/ml})}{\text{Weight Sample (g)}} \times 10^{-4}$$

## 8 REFERENCES

- 8.1 Houdashelt, Leisa (1995) Master's Thesis "Evaluation of Methods for the Determination of Ammonia in Glass Cleaners and other Consumer Products" University of California, Davis.
- 8.2 Standard Methods for the Examination of Water and Wastewater" 17th Ed. 4500-NH<sub>3</sub> "Ammonia-Selective Electrode Method".
- 8.3 Orion Instruction Manual Model 95-12 Ammonia Electrode (1990).

## Appendix A

### Operation of the ORION 920A

NOTE: Check the membrane, if a significant length of time has past since the previous analysis, the membrane should be changed. To replace the membrane, remove the cap at the end of the probe and remove the old membrane. Place a new membrane over the tip of the probe and replace cap carefully so that the membrane does not wrinkle. (See manual) Unscrew the top of the probe where the lead wire comes in, fill the probe body with 2.5 mL of electrode filling solution and replace the top of the probe.

1. The instrument stays in the STANDBY mode.....STANDBY PRESS ANY KEY  
Press a key and the display screen should read:

0.000 CON  
1-NH3 25° C RDY

If something other than NH3 is in channel 1 (probably pH) press 2<sup>nd</sup> ELECTRODE ID (green keys). Scroll through by pressing NO, until 9-NH3 appears, press 9 and YES. If the mode is other than concentration, press 1st MODE (white keys), scroll through until have CON appear.

2. The calibration standard used for the ammonia determination is Alltech, a 999  $\mu\text{g/mL}$  (1000  $\mu\text{g/mL}$  NIST traceable) stock solution of ammonium kept in the refrigerator. A 3-point calibration is done.
3. To calibrate, press 1st CALIBRATE. Screen will display the last date and time of calibration. Then the number of standards is asked, ENTER NO STDS, press 3, YES. Now the screen will read: 1-NH3 25°C STD1
4. To a 100 mL volumetric flask add about 80 mL of deionized water, using an Eppendorff pipettor, pipet 100  $\mu\text{L}$  of the ammonium standard into the flask and bring to volume with deionized water. Transfer the solution into a 150 mL beaker and placing a stir bar in the beaker, place on the stir plate and insert the probe into the solution. Using a Rainin 2.5 mL pipettor, pipet 2.0 mL of ionic strength adjusting solution (ISA) to the beaker of standard.
5. The screen will indicate that the standard is being measured, MEAS. This may take several minutes before the display stabilizes, when complete the screen will read:

READY ENTER VALUE.

Enter 1.0, YES, this is the concentration of the first standard.

6. The screen will now read: 1-NH3 25°C STD2

For the next standard (5.0  $\mu\text{g/mL}$ ) pipet 400  $\mu\text{L}$  of the standard into the same beaker. No ISA is added this time, the solution should still be blue. The probe will again take several minutes before obtaining a stable reading, then the READY ENTER VALUE will be displayed. Press 5.0, Yes.

7. The screen now reads: 1-NH3 25°C STD3.

To the same solution, pipet 500  $\mu\text{L}$  of the standard ( 1.0 mL total). When ready, press 10.0, YES.

8. The calibration is complete, the instrument will print out the report and determine the slope. The slope should be approximately -56.0mV. (-55.0-59.0 mV acceptable).
9. If the slope is not within the acceptable range, recalibrate with fresh solutions. Started from step #4.
10. As check of the calibration is made using 1000/ $\mu\text{g/mL}$  solution from EM Science. Add 0.5 mL of the stock solution to 80 mL of deionized water in a 100 mL volumetric and bring to volume. Transfer into a 150 mL beaker with a stir bar, place on the stir plate, insert the probe, and add 2.0 mL of the ISA solution. After a few minutes the display concentration should read 5.00. Control limits are  $\pm 3s$  of the historical average of 5.0. Press 1st PRINT to print out the value.
11. If the slope is good and the 5.0  $\mu\text{g/mL}$  check is within the controls, now ready to run samples. The display should be reading: 1-NH3 25°C RDY
12. The samples are prepared as a 1:1000 dilution in 100 mL. The dilution is made with the 1:10 dilutions made of the samples in MPA. In a 100 mL volumetric flask add approximately 80 mL of deionized water. Using an Eppendorff pipettor, pipet 1ml of the sample into the volumetric and bring to volume. Transfer into a 150 mL beaker, with a stir-bar, place in the stir plate, insert the probe. Add 2.0 mL of the ISA solution. The display will read:

1-NH3 25°C MEAS

When complete the display will read RDY. Press 1st PRINT, to record.

13. A standard addition is made to check that the probe is reading accurately and that there are no interferences with the analysis. To the solution add 0.5 mL of the ammonium standard that is used for the check (EM Science). After the reading has stabilized, the display should read the 5.0 standard plus the reading obtained for the sample. Press 1st PRINT to record and indicate this is a standard addition.



14. If the 5.0 standard is not recovered, then it is possible that there has been some interferences in the sample. This is particularly the case with the presences of compounds that will wet the membrane, and therefore cause its failure. Check the tip of the probe to observe the condition of the membrane. If the membrane looks wet, the membrane will have to be replaced. Make a note of which sample caused the membrane failure, it is probable the ammonium will have to be determined by ion chromatography.
15. If the membrane has failed, then it must be replaced as described above and the instrument recalibrated. Re-analyze the sample that was causing the problem, if the membrane fails again record in the lab notebook that this sample caused membrane failure and was not analyzed. Continue with samples, to each the standard addition is made. To record values press 1st and PRINT.
16. After the samples are completed, run the 5.0  $\mu\text{g/mL}$  check again to confirm the operations of the probe. Record all data in the lab notebook as shown on the example page.
17. Upon completion of the analysis make certain the probe is rinsed with deionized water and placed in a beaker of water for storage. The instrument will go in the STANDBY mode automatically.
18. Calculations:

Example: Reading on the display gives 1.0, sample is 1.0  $\mu\text{g/mL}$ .

This is a dilution of  $10^3$ , or 1.0 mg/mL. As percent:  $0.001 \text{ g/mL} \times 100 = 0.1\%$ .

### **Ammonium Determination**

Ammonium has the potential to be counted as a voc in the total volatiles analysis as determined in SOP ES01. Ammonium is quantitated as ammonia at concentrations equal to or greater than 0.1% and subtracted from the total voc content.

In the presence of basic pH, the ammonium ion in solution is converted to dissolved ammonia, which diffuses through the hydrophobic gas permeable membrane of the electrode. The partial pressure of ammonia of any given sample once equilibrated will be proportional to the concentration of ammonium. A known amount of ammonium is then added to the sample and the concentration determined again.

## SOP REVISION HISTORY

1. August 20, 1996: The samples will be prepared from the 1:10 dilutions in MPA. The samples are weighed 1.0 mL aliquots to 10 mL in MPA and 1.0 mL of this dilution is prepared for the ammonia analysis.
2. March 10, 1998. Adjusted document font to Times New Roman 12. Inserted appendix A. This was formerly a stand-alone document.